JOURNAL OF MATERIALS SCIENCE 24 (1989) 2999-3001

X-ray characterization of SnTe: Gd crystal

ZBIGNIEW GOŁACKI, GABRIEL JASIOŁEK
Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

Electron probe microanalyses were performed on SnTe crystal grown by the Bridgman method doped with 1.8 wt% Gd. Scanning electron microscopic observations and electron probe microanalysis carried out on the (1 1 0) and (1 0 0) oriented samples revealed two types of precipitate enriched in gadolinium. It was suggested that the dominant type contained a mixture of Gd_4Te_7 phase and $Te_{0.8}Gd_{0.2}$ eutectic. The composition of the second precipitate type was found to be a eutectic enriched with gadolinium.

1. Introduction

SnTe crystals belong to the cubic materials with an average of five electrons per atom [1]. Their properties, such as narrow band gap, ferroelectricity and thermopower, attract great interest from physicists. On the other hand, ternary alloys of $Sn_{1-x}M_xTe$ type, where M is 3d or a rare earth element, are "magnetic diluted semiconductors" [2]. They have been intensively investigated; it has been shown that manganese has a much stronger effect on the magnetic properties of these mixed crystals [3, 4] than do gadolinium and europium [5–8]. In many cases only a little information is available about the limit of solubility of the M element in the SnTe matrix, the kind, amount and characterization of inclusions. Interpretation of the results of the electrical and magnetic measurements needs detailed knowledge of the real structure of crystals and identification of eventual inclusions. Sometimes doping of rare earths to the semiconducting compounds involves the formation of precipitates enriched with rare earth elements [9]. Therefore, a careful examination was made of the sample composition for SnTe:Gd crystal. The present paper aims to discuss the most probable phase compositions of the precipitates in this crystal.

2. Samples

99.999% pure tin and tellurium and 99.9% pure gadolinium were the starting materials in the crystal growth. First SnTe was synthesized and then SnTe, gadolinium and tellurium were placed in a silica glass ampoule with graphitized walls of 12 mm inner diameter and a conical tip. The crystal used for our investigations consisted of 0.944 g Gd, 1.149 g Te, which corresponds to stoichiometric Gd_2Te_3, and 50 g SnTe. After evacuation to 10^{-5} torr the ampoule was sealed and placed in a vertical furnace for 3 d at 1100° C to homogenize the load, and then was lowered to the cold end at a speed of $20\,mm\,d^{-1}$. The temperature gradient at the crystallization surface was $50°\,C\,cm^{-1}$. The growth process finished at the moment when the ampoule emerged from the furnace and reached room temperature. After the process slices were cut perpendicularly to the growth axis, lapped flat and polished with diamond paste. The surfaces quasi-parallel to the (1 1 0) crystallographic plane were exposed. A few samples were cleaved to reveal the (1 0 0) planes.

3. Experimental procedure

The samples were exposed to an electron beam in the JXA-50A electron probe microanalyser (EPMA). An accelerating voltage of 25 kV and a beam current of 12 nA were used. The depth of X-ray generation was 2.1 μm. For the quantitative analysis of the sample compositions, Johann spectrometers were applied. A LiF analysing crystal (interplanar distance $d = 0.201\,35$ nm) [10] for the Gd$L\alpha_1$ line and a PET analysing crystal ($d = 0.440$ nm) for the Sn$L\alpha_1$ and Te$L\alpha_1$ lines were used. A ZAF correction procedure was included during the quantitative analysis. For the X-ray emission spectroscopic studies (XES) a step by step registration of the $L\gamma_4$ spectrum (electronic transition 5p to 2s) of tellurium, with a resolution equal to 0.28 eV, was performed with the LiF crystal spectrometer.

4. Results

Scanning electron microscopic observations carried out on the (1 1 0) oriented surfaces revealed the grain structure of the crystals and the regions containing a large number of precipitates elongated in one crystallographic direction within a given grain. These precipitates occurred in the samples starting from the initial lower part of the crystal. The number of precipitates decreases along the growth direction, the upper part of the crystal being free of precipitates. The direction mentioned was detected to be parallel to the [1 0 0] crystallographic direction. These precipitates, P1, consisted of gadolinium (Fig. 1a) and tellurium. X-ray mapping did not reveal tin in these precipitates (Fig. 1b). The width of these precipitates was $< 4\,\mu$m.

Cleavage of a crystal made SEM observations for the (1 0 0) oriented surfaces possible. A few individual precipitates in the form of plates were found. These precipitates contained gadolinium (Fig. 2a). The X-ray map made by SEM does not show tin (Fig. 2b) but revealed a small amount of tellurium (Fig. 2c). Close

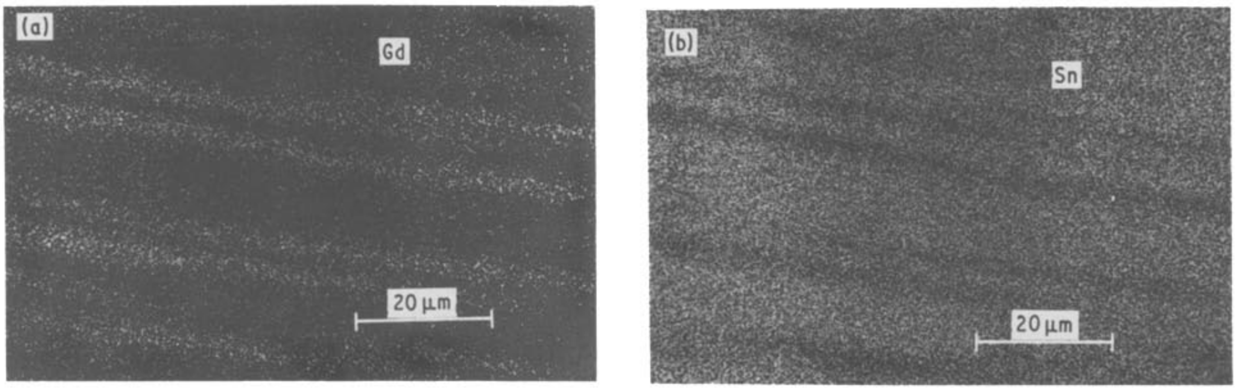


Figure 1 X-ray maps of (a) gadolinium and (b) tin distributions on the (1 1 0) oriented surface of an SnTe : Gd sample.

to these precipitates, P2, precipitates of the P1 type were also observed (lower part of Fig. 2). The diameter of the largest P1 precipitates reached 20 μm and that of the P2 type 40 μm.

The size of the precipitates visible on the (1 1 0) surfaces was comparable with the X-ray resolution. Thus, quantitative analysis of their composition was difficult because of the matrix composition influence. Therefore, quantitative analysis of the chemical composition of the precipitates of both types was performed on the (1 0 0) oriented surfaces. It was found that the composition of the P1 precipitates can be expressed by the formula $\mathrm{Gd}_{0.340}\mathrm{Sn}_{0.015}\mathrm{Te}_{0.645}$. For the P2 precipitates the composition was ascertained to be $\mathrm{Gd}_{0.856}\mathrm{Sn}_{0.015}\mathrm{Te}_{0.134}$. In the matrix the mean gadolinium concentration was estimated to be 4.2(5) at % (the sensitivity of the measurements is shown in parentheses). A value of 7.0 at % was detected close to the grain boundaries. For the matrix and grain boundaries the concentration of tellurium was found to be 49.5 at %. Values of 46.3 and 43.5 at % for the tin concentration were found in the matrix and at the grain boundaries, respectively.

XES study of P1 precipitates showed that the half-width of the main maximum of the $\mathrm{Te}L\gamma_4$ spectrum is wider by 0.42 eV than the half-width registered for the matrix. As a reference sample for the XES measurements, a $\mathrm{Pb}_{0.6}\mathrm{Sn}_{0.4}\mathrm{Te}$ crystal containing large areas of a $\mathrm{Te}_{0.87}\mathrm{Sn}_{0.08}\mathrm{Pb}_{0.05}$ eutectic was used. The considered half-width for the P1 precipitates was the same as for the (PbSn)Te crystal. A value larger by 0.56 eV than for the SnTe matrix was ascertained for the P2 precipitates and in the case of the Te(Sn, Pb) eutectic. Furthermore, a curvature in the low energy side of the spectrum of the P1 precipitates, at a distance of 5.6 eV from the main maximum position, was found.

5. Discussion

Assuming that the matrix lying under the thin precipitates has an influence on the results obtained, the contribution of tin can be removed. Taking into account the mass absorption coefficient for $\mathrm{Sn}L\alpha$ radiation, 455 $\mathrm{cm}^2\,\mathrm{g}^{-1}$ in Te and 895 $\mathrm{cm}^2\,\mathrm{g}^{-1}$ in Gd, as well as that of the $\mathrm{Te}L\alpha$ radiation, 415 $\mathrm{cm}^2\,\mathrm{g}^{-1}$ in Te and 701 $\mathrm{cm}^2\,\mathrm{g}^{-1}$ in Gd [11], the 2 at % contribution of tellurium should also be removed from the incident results. Then, the results devoid of the matrix influence would be as follows: $\mathrm{Gd}_{0.35}\mathrm{Te}_{0.65}$ for the P1 precipitates (Te/Gd concentration ratio = 1.857) and $\mathrm{Gd}_{0.88}\mathrm{Te}_{0.12}$ for the P2 precipitates (Gd/Te concentration ratio = 7.33).

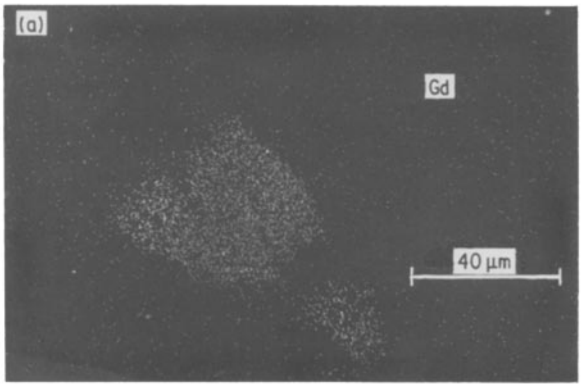
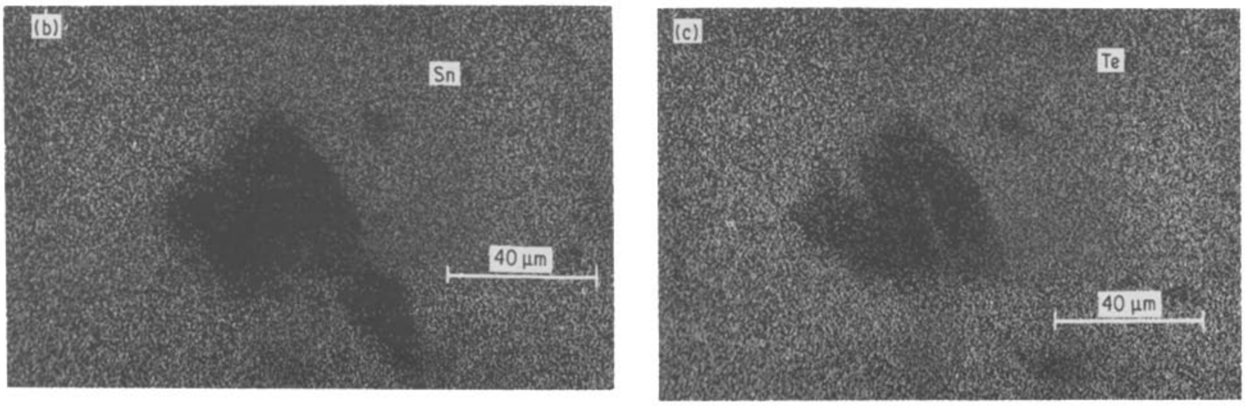


Figure 2 X-ray maps of (a) gadolinium, (b) tin and (c) tellurium distributions on the (1 0 0) oriented surface of an SnTe : Gd sample.



The results obtained suggest that the component of the P1 precipitates is most probably Gd_4Te_{7+x} or $GdTe_{2-y}$. An analogy with the La–Te compounds shows that the melting point for the Gd_4Te_{7+x} phase is higher than for $GdTe_{2-y}$ [12, 13]. Thus, the first phase is more probable. Eutectics rich in tellurium are also possible. Therefore, finally the composition of the P1 precipitates can be written $Gd_4Te_7 + Te_{0.8}Gd_{0.2}$. This gives the required proportion 1.857 between tellurium and gadolinium. Similarity to the Pr–Se compounds was also taken into consideration. As reported by Kost *et al.* [12], the eutectic rich in gadolinium usually contains about 7 to 9 at % Te. Assuming that for the Gd–Te system such behaviour is valid for the P2 precipitates, the sum shown below can be applied:

$$Gd_{0.93}Te_{0.07} + Te_{0.8}Cd_{0.2}$$

where the eutectic rich in tellurium also appears, as the common system for both precipitate types.

Following an earlier work [6], the model of the occupancy of the vacancies connected with the 1.5 at % Sn in SnTe material by gadolinium may be taken into consideration. However, the detection of about 4 at % Gd indicates the need to consider an additional interaction mechanism of gadolinium with the SnTe lattice. It has been proposed [6, 8] that the solid solution of the $(SnTe)_{1-x}$–$(GdTe)_x$ type describes this interaction. SnTe and LnTe belong to compounds with the Pm3m structure type (NaCl type). The lattice constant of each LnTe is close to the SnTe lattice constant [14]. Therefore, such a solid solution seems reasonable. On the other hand, to link the suggestion about the location of gadolinium with the presence of the P1 and P2 precipitates we propose that the 2.5 at % excess gadolinium above the amount located in the tin vacancies could be treated as submicrometric precipitates of the Gd_4Te_7 phase. This phase has a melting point lower than that of the GdTe phase [12]. The Gd_4Te_7 phase, similar to the Dy_4Te_7 compound, should have the P4/mbm tetragonal structure [14]. For the Ln_4Te_7 compounds, the c/a ratio of the lattice parameters is larger than 2.0. If this alternative model is valid, the (1 0 0) planes should be treated as nucleus planes for the tetragonal phase. The shape of the precipitates observed is in good agreement with the model proposed. Segregation of these precipitates could be compared to the increase of the gadolinium concentration at the grain boundaries.

Taking into account the width of the 2s shell of tellurium, 2.5 eV [15], and the partial density of state of SnTe [1], the width of the 5p tellurium contribution in the P1 precipitates density of state at the top of the valence was ascertained to be 3.0 eV. For the P2 precipitates the 5p shell width was estimated to be 3.2 eV. The curvature at 5.6 eV in the lower energy part of the $L\gamma_4$ spectrum of tellurium in the case of the P1 precipitates is caused by the cross transition 4f electrons of gadolinium to the 2s shell of tellurium. This transition confirms the phase character of the P1 precipitates. Similarity between the character of the Te$L\gamma_4$ spectrum revealed for the P2 precipitates and the Te(Pb, Sn) eutectic strongly indicates the eutectic character of the P2 precipitates.

The results obtained allow us to conclude that doping of SnTe with up to 1.8 wt % Gd leads to the appearance of precipitates enriched with gadolinium. One type of these precipitates consists mainly of the Gd_4Te_7 phase and the second one contains mainly of the $Gd_{0.93}Te_{0.07}$ eutectic. Both types of precipitate also contain the $Te_{0.8}Ge_{0.2}$ eutectic.

Acknowledgements

The authors thank Mr J. Makowski for the sample orientations. This work was supported partially in the framework of Program CPBP 01.20.3.

References

1. H. POLATOGLOU, G. THEODOROU and N. A. ECONOMOU, *Phys. Rev.* **B33** (1986) 1265.
2. J. K. FURDYNA, *J. Appl. Phys.* **53** (1982) 7637.
3. M. ESCORNE, M. GODHINO, J. L. THOLENCE and A. MANGER, *ibid.* **57** (1985) 3424.
4. A. MANGER and M. ESCORNE, *Phys. Rev.* **B35** (1987) 1902.
5. H. T. SAVAGE and J. J. RHYNE, *AIP Conf. Proc.* **5** (1971) 879.
6. Y. S. FIEYSEYEV and Y. N. NASIROV, *Nieorg. Mater.* **7** (1971) 506.
7. P. URBAN and G. SPERLICH, *Solid State Commun.* **16** (1975) 927.
8. F. M. KAMARLY and A. YU. YANGIROV, *Phys. Status Solidi (a)* **101** (1987) K61.
9. G. JASIOŁEK, J. RACZYŃSKA and J. GÓRECKA, *J. Cryst. Growth* **78** (1986) 105.
10. K. F. J. HEINRICH, in "Electron Beam X-Ray Microanalysis" (van Nostrand Reinhold Company, New York, 1981) p. 101.
11. B. L. HENKE, in "X-Ray Data Booklet" edited by D. Vaughan (LBL University of California, Berkeley, 1985) pp. 2–32.
12. M. E. KOST, A. L. SHILOV, V. I. MICHEYEVA, C. I. USPIENSKAYA, V. I. NOVOSHONOV, K. E. MIRONOV, M. N. ABDUSALIAMOVA, A. A. YELISIEYEV, G. M. KUZMICIEVA and G. B. SEIFER, "Sojedinienija Redkoziemielnych Elementov" (Nauka, Moskva, 1983) p. 184.
13. J. FLAHAUT, in "Handbook on the Physics and Chemistry of Rare Earths", edited by K. A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1979) p. 66.
14. B. EISENMANN and H. SCHÄFER, in "Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology", edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1986) pp. 9, 413.
15. K. D. SEVIER, in "Low Energy Electron Spectrometry" (Wiley Interscience, New York, 1972) p. 220.

Received 3 May
and accepted 9 September 1988